OBSERVATIONS ABOUT THE STRUCTURE OF ALKALI SILICATE GLASSES AND MELTS AFTER THE INSERTION OF OH GROUPS

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1. Report No. NASA TT F-16,270	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle OBSERVATIONS ABOUT THE STRUCTURE OF ALKALI SILICATE GLASSES AND MELTS AFTER THE INSERTION OF OH GROUPS	5. Report Date May, 1975
	6. Performing Organization Code

7. Author(s) H. Franz and T. Kelen	8. Performing Organization Report No.
	10. Work Unit No.

9. Performing Organization Name and Address SCITRAN Box 5456 Santa Barbara, CA 93108	11. Contract or Grant No. NASw-2483
	13. Type of Report and Period Covered Translation

12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546	14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

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17. Key Words (Selected by Author(s))	18. Distribution Statement Unclassified – Unlimited

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 27	22. Price

OBSERVATIONS ABOUT THE STRUCTURE OF ALKALI SILICATE GLASSES AND MELTS AFTER THE INSERTION OF OH GROUPS *

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Communication from the Max-Planck-Institute for
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SUMMARY: Electron/theory predicts regularities for the
alkali distribution in binary alkali silicate glasses and
for the reaction of water vapor with the silicate melt.
The dissolved water is installed as OH groups, the bond-
state of which is a very sensitive indicator for the
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such as generation of alkali "swarms" and occupation-
state of the single [SiO_4] tetrahedron by alkali ions are
discussed using the infrared spectra of water-containing
glasses.

1. PROBLEM FORMULATION

A series of publications about the solubility and the installa-
tion of water or water vapor, respectively, in glasses and glass

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* Reported by H. Franz to the professional committee I of the
   DGG on April 21, 1966, in Würzburg.
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*** Numbers in margin indicate pagination in original foreign text.

melts has appeared during the last 10 years. In most of the cases the authors tried to draw conclusions from their results of measurements about the mechanism of the reaction of water vapor with the glass or the melt. From the solubility equation

$$c_{H_2O \text{ dissolved}} = k \cdot (p_{H_2O})^{1/2} \qquad (1)$$

which was found by Walsh and collaborators [1] with slag and by several other authors [2 to 11] with different glass compositions, one can deduce that H_2O melts of oxides are not molecularly dissolved but are cleaved into two parts during the solubilization process. This notion is supported by the results of Scholze [5], who could prove by infrared spectroscopy that water dissolved in glasses exists exclusively in the form of OH-groups.

In a previous publication [9], the relation between water vapor solubility and the melt's basicity, was demonstrated. A discussion of possible reaction equations for the reaction of the H_2O molecule with the oxygens in different bond-states (bridge-oxygens, hole-oxygens, free oxygen ions) was deliberately abandoned. The reaction was formulated in a general way as an ion equation:

$$H_2O_{(Gas)} + O^{2-}_{(Melt)} \rightleftarrows 2\ OH^-_{(Melt)} \qquad (2)$$
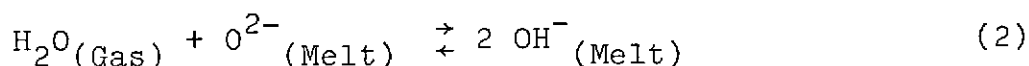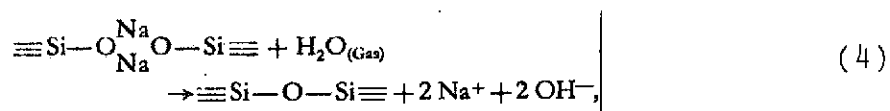
and the solubility considered as a function of the average activity of the oxygens in all bond-states. However, in the literature the different reaction possibilities are also discussed. Moulson and Roberts [7], Adams and Douglas [12] and Hetherington and Jack [8] assume the following mechanism for the reaction of water vapor with silica glass:

$$\equiv Si-O-Si \equiv + H_2O \rightarrow \equiv Si-OH + HO-Si \equiv . \qquad (3)$$
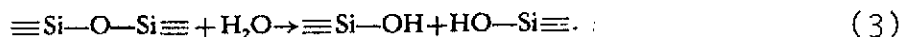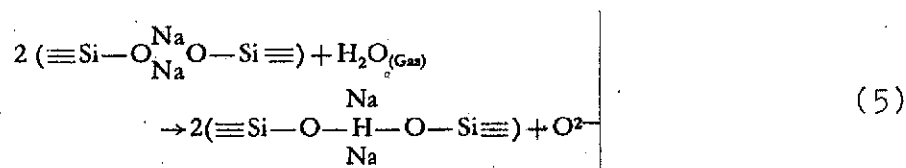
This formulation is also reported by Tomlinson [2], Russell [3], Kurkjian, and Russell [4], Scholze [5], and by Uys and King [13], also for the reaction of water vapor with silicate glasses, however, partially restricted to systems which are low in alkali. This mechanism also explains the network-cleaving effect of dissolved water, which becomes manifest by the lowering of the viscosity, as one can see from the literature.
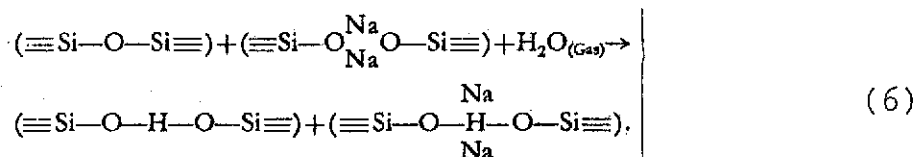
For glass melts with higher contents of network modifiers different reaction mechanisms are proposed. Kurkjian and Russell [4] assume the following course of the reaction:

$$\equiv Si - O^{Na}_{Na} O - Si \equiv + H_2O_{(Gas)}$$
$$\rightarrow \equiv Si - O - Si \equiv + 2\,Na^+ + 2\,OH^-, \tag{4}$$

in part also

$$2\,(\equiv Si - O^{Na}_{Na} O - Si \equiv) + H_2O_{(Gas)}$$
$$\rightarrow 2(\equiv Si - O - \overset{Na}{\underset{Na}{H}} - O - Si \equiv) + O^{2-} \tag{5}$$

or

$$(\equiv Si - O - Si \equiv) + (\equiv Si - O^{Na}_{Na} O - Si \equiv) + H_2O_{(Gas)} \rightarrow$$
$$(\equiv Si - O - H - O - Si \equiv) + (\equiv Si - O - \overset{Na}{\underset{Na}{H}} - O - Si \equiv). \tag{6}$$

According to Equation (4) which is also applied to systems with high alkali contents by Uys and King [13], a Si—O—Si— bridge would be created by the reaction of a separation site with water vapor, which seems unlikely. The reactions (5) and (6) which, moreover, should still be possible, accommodate the OH-groups with strong hydrogen bonds, which were proven by Scholze [5] to exist in such glasses. Adams and Douglas [12] set up the following reaction equation:

$$2\,(\equiv\!Si\!-\!O\!-\!Si\!\equiv) + Na_2O + H_2O \rightarrow$$
$$2(\equiv\!Si\!-\!OH\cdots O^-\!-\!Si\!\equiv).$$
$$Na^+$$
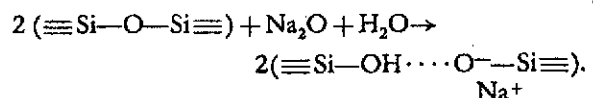
The Equations (3) to (7) show, strictly formally, possibilities of reaction of the water molecule with the silicate melt, but do not allow any statements about the course of the reaction and its regularities. In the following we will attempt to investigate these regularities on the basis of electron theory which was applied to the silicate bond by Noll [14]; we also want to demonstrate the connections between the structure of the glasses and the infrared absorption of the OH-groups in silica glass and silicate glasses.

2   SILICA GLASS

The essential elements of the SiO_2 glass are $[SiO_4]$-tetrahedrons which are connected to an irregular, three-dimensional network via common oxygen vertices. In the molten condition, these Si—O—Si- bonds are more or less activated by thermal excitation and because of their irregular near environment. In the reaction with water vapor, the attack will most likely occur at the momentarily weakest bond.
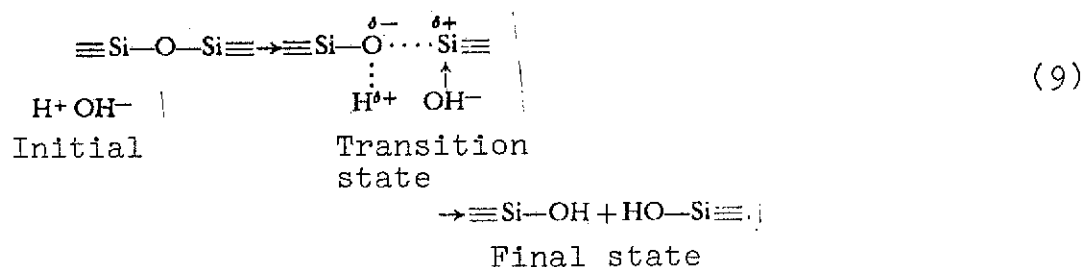
During its entry into the melt, the water molecule is cleaved into two units, as was shown in the introduction. One may assume that a dissociation according to

$$H_2O \rightarrow H^+ + OH^- \tag{8}$$
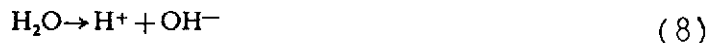
occurs. As the primary step of the hydrolytic cleavage of the Si—O—Si-bond, two possibilities are theoretically conceivable:

a)   addition of the proton at the reactive oxygen anion and

b)   addition of the hydroxyl ion at the silicium cation.

According to Weyl [15] mechanism a) is favored if polar-
izable anions are present; on the other hand, b) is favored if the
cation can widen its coordination which is very unlikely in the
very stable tetra-coordinated silicium cation in usual silicate
glasses. One therefore has to assume that the hydrolysis reaction is
initiated by a proton addition at the bridge-oxygen according
to a), with subsequent cleavage of the Si—O-bond and filling of
the free valence at the Si-cation by the hydroxyl group:

$$\equiv Si-O-Si\equiv \;\rightarrow\; \equiv Si-\overset{\delta-}{O}\cdots\overset{\delta+}{Si}\equiv \qquad (9)$$

$$H^+ OH^- \qquad\qquad H^{\delta+}\;\; OH^-$$

Initial   Transition
state

$$\rightarrow\; \equiv Si-OH + HO-Si\equiv$$

Final state

The OH-groups created herewith, however, are not strictly
monomeric (as e.g., in the case of triphenyl sinanol in very
dilute solution) but they can form hydrogen bonds to adjacent
oxygens, that is, to bridge-oxygens at the same and at adjacent
tetrahedrons and to oxygens of neighboring OH-groups (bonding
type A). The strength of these H-bridges, however, will be very
small because these partner-oxygens are already strongly polarized
by the neighboring strong cations Si^{4+} and H+, respectively, and,
therefore, have little affinity to the bridge bond. The bond
strengths of the different H-bridges depend on the polarization
state of the partner-oxygen in question and therefore, will differ
somewhat, whereby one has to take into account a further different-
iation because of the different O-O distances.

The monomeric triphenyl silanol

$$\left[\begin{array}{c} \text{Ph} \\ | \\ \text{Ph}\!-\!\text{Si}\!-\!\text{OH} \\ | \\ \text{Ph} \end{array} \right]$$
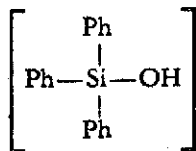
shows a sharp stretching frequency band at 2.72 μm. In the
spectrum of the SiO_2-glass, the strength of the H-bridges is too
small; however, the position of the OH-stretching frequency band may
be shifted insignificantly to larger wavelengths. Moreover,
a broadening of the OH-stretching frequency band is expected because
of the small energy differences of the single oscillators. Since
all H-bridges lead more or less to a weakening of the OH-bond, a
broadening of bands can only occur in the direction to larger
wavelengths, whereby the OH-band becomes asymmetrical. These con-
siderations are confirmed by Figure 1 where IR-spectra of triphenyl
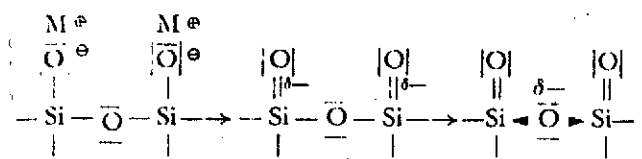silanol and silica-glass are compared.

3. BINARY ALKALI SILICATE GLASSES

3.1. Water-free systems

During cleavage of a Si—O—Si-bond in a SiO_2-melt by one
molecule of R_2O, the primary step (in analogy to the H_2O-attack)
might be the addition of a cation R+ to the bridge-oxygen, whereby
the attack will occur at the bond which is favored at that moment.
The assumptions change, however, if alkali hole-sites are already
present. As demonstrated by Noll [14], the Si-O-bond has to be
considered as resonance bond of covalent, polar, and double bond
contributing forms. The metal atom M at the separation-site has
less attractive force on the electrons of the separation-site
oxygen than the silicium atom because of its smaller electro-
negativity, so that it acts as electron "donor" in respect to it.
In the bond Si—O(→M) the covalent and double bond proportions

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are thereby enhanced. This leads to an increase of the polar
proportions in the neighboring bond Si—O(→Si), which entails
that the bridge-oxygen enhances there its negative formal charge
δ and thereby its polarizability and reactivity to a cationic
attack. These effects are the stronger the more the electro-
negativities of M and Si differ, i.e., the larger the donor
effect of M against Si is (scheme according to Noll [14]):   /143

$$\begin{array}{cccccc}
\overset{\text{M}^{\oplus}}{\overset{|}{\underset{|}{\text{O}}}}{}^{\ominus} & \overset{\text{M}^{\oplus}}{\overset{|}{\underset{|}{\overline{\text{O}}}}}{}^{\ominus} & \overset{|\text{O}|}{\overset{||^{\delta-}}{}} & \overset{|\text{O}|}{\overset{||^{\delta-}}{}} & \overset{|\text{O}|}{\overset{||}{}}{}^{\delta-} & \overset{|\text{O}|}{\overset{||}{}} \\
-\text{Si}-\overline{\text{O}}-\text{Si}\longrightarrow & --\text{Si}-\text{O}-\text{Si}\longrightarrow & -\text{Si}\blacktriangleleft\overline{\text{O}}\blacktriangleright\text{Si}-
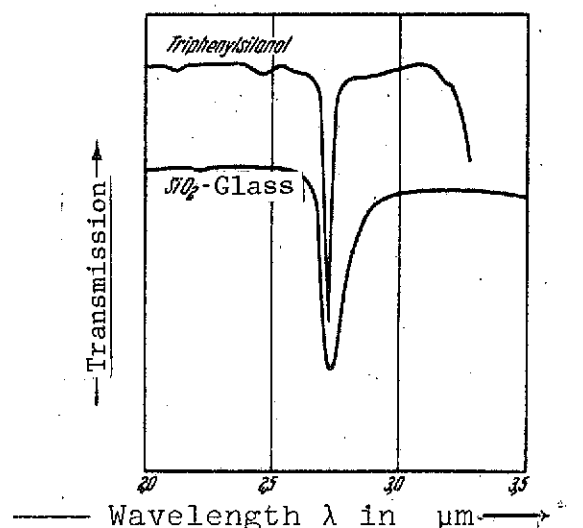\end{array}$$

Donor effect of M against Si increasing

Figure 1. Comparison of the OH-band in the IR spectra of tri-
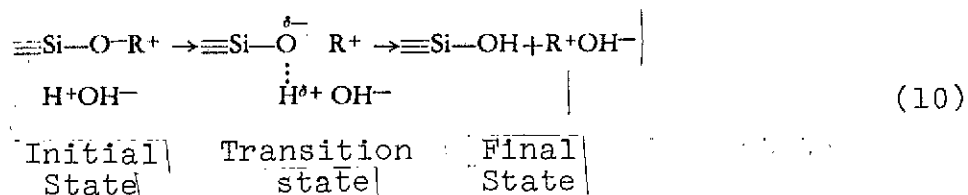phenyl silanol. (0.025 Mole/l in CCl_4 and SiO_2-glass (d= 0.6 mm).

If these conclusions are transferred to the glass structure,
one recognizes that by an alkali separation site at one vertex
of a [SiO_4] tetrahedron , the negative charge of the other bridge-
oxygens of the same tetrahedron is increased. The attack of
another alkali cation will therefore occur at such a bridge-
oxygen which has become more easily polarizable because of the
neighboring separation site.

The accumulation of alkali at one tetrahedron is thereby indeed favored, but at the same time, the local offer of reactive alkali oxide decreases with every bound alkali ion. Probably the mutual repulsion of the cations with like charges also plays a role in the counter-current influence. This way it has to necessarily result in an equilibrium state in which all four filling steps of a $[SiO_4]$ tetrahedron by alkali ions show a certain probability. The quantitative situation will be treated in more detail in Section 3.6.

3.2. The reaction with water vapor

In Section 2, the mechanism of attack of water in the SiO_2-system was described. In a binary alkali silicate melt, different suppositions exist insofar as the proton attack can here occur at two differently polarized oxygen atoms, which are generally designated as bridge-oxygens (a) or oxygens bound to an Si (b):

a) at the oxygen in the Si—O—Si-bond, according to Equation (9),

b) at the oxygen in the Si—O—R+-group, according to Equation (10):

$$
\begin{array}{ccc}
\equiv\!Si\!-\!O^-R^+ \rightarrow \equiv\!Si\!-\!\overset{\delta-}{O}\ R^+ \rightarrow \equiv\!Si\!-\!OH\!+\!R^+OH^- \\
H^+OH^- \qquad\qquad \overset{..}{H}{}^{\delta+}OH^- \\
\text{Initial} \qquad \text{Transition} \qquad \text{Final} \\
\text{State} \qquad\quad \text{state} \qquad\quad \text{State}
\end{array}
\qquad (10)
$$

The reaction according to Equation (10) leads to an ion exchange $R^+ \longleftrightarrow H^+$. The exchanged alkali ion, with the hydroxyl ion as partner, will, analogously to the proton, either cleave a Si—O—Si-bond or it will evaporate. The literature [6, 16-18] shows that the evaporation of alkali from silicate melts increases rapidly with decreasing field strength and increasing alkali ion

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concentration, and also with the partial pressure of the water vapor. This points to the attainment of an equilibrium between the competing reactions (9) and (10) which is determined by the composition of the glass. In accordance with the electron theory, this equilibrium is shifted in the direction of (9) at a high field strength of R+ (weak donor effect against Si), but in the direction of (10) in case of a low field strength of R+ (strong donor effect against Si).

3.3. The OH-groups in the glass structure

According to reaction Equation (9), as well as according to (10), ═ Si-OH-groups are created in the glass structure, which can form hydrogen bonds to the oxygens of their closest surrounding. The following five basic types theoretically result thereby from the structure:
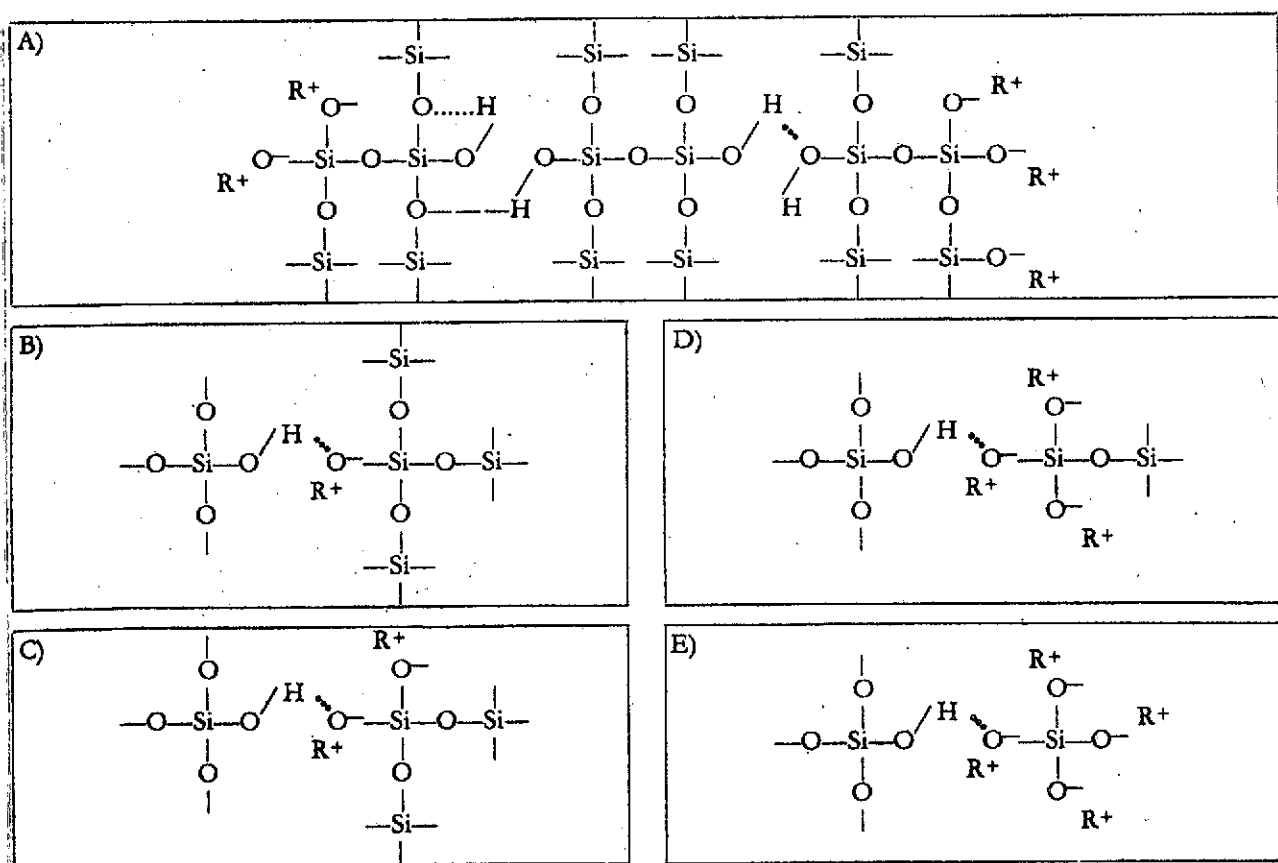
The OH-stretching frequency bands at 2.8, 3.6 and 4.25 μm
which appear in the infrared spectra of the alkali silicate
glasses and which can be seen in Figure 2, have to be assigned
to these different types of bonds. The curves shown here repre-
sent the difference between the IR-spectra of two samples of
the same glass, which differ only in their water content. In this
way, the primary absorptions of the water-free glasses could be
eliminated, which influence the spectra especially in the region of
the second and third band and which make the recognition of the
third band in many cases difficult.

Scholze [5, 19], could show that the first band at 2.8 μm
is caused by free OH-groups; the second band at 3.6 μm is caused
by OH-groups with hydrogen bonds to neighboring singly bound
oxygens, and the third band by the hydrogen bonds which bind
isolated [SiO$_4$]-tetrahedrons to the residual network.

One can easily recognize that the first band at 2.8 μm
originates from the bonding type A. In this case, the OH-groups—
in analogy to the silica glass — can only form very weak H-
bridges to oxygens which are bound to two Si, or to Si and H,
respectively. The polarizability of these partner-oxygens can
be|influenced in many ways by alkali separation sites, which
exist in the neighborhood, so that a broad spectrum of the hydro-
gen bond energy is created. Thereby the first OH-band broadens
with increasing alkali content and is simultaneously shifted to
longer waves, as shown in Figure 3.

The types B,C,D, which differ only by the number of the
additional R+ cations at the same tetrahedron, correspond to a
hydrogen bond to singly bound oxygens. This tetrahedron is
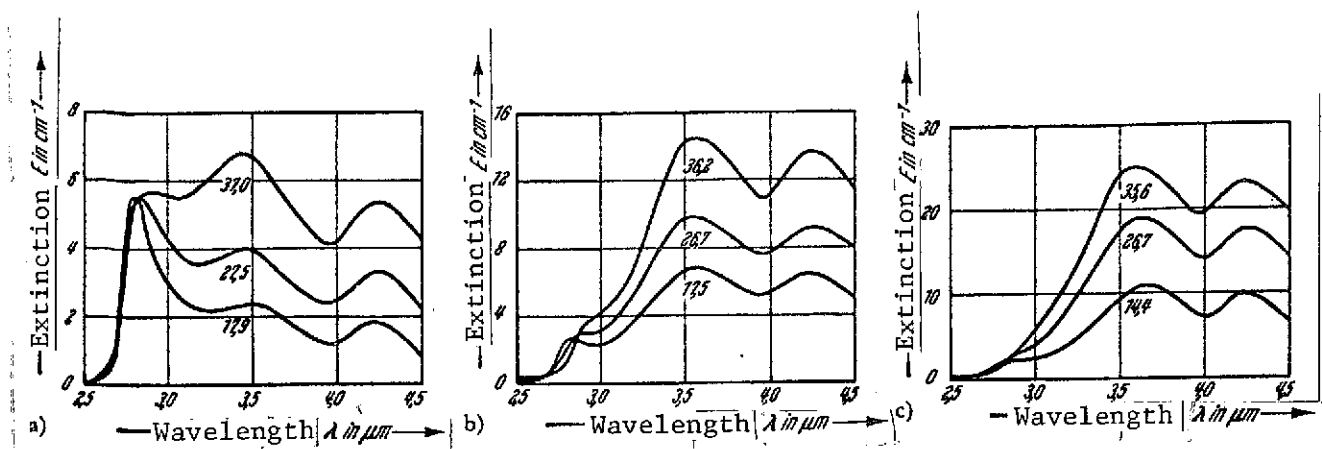connected with the residual network via at least one Si—O—Si-
bridge.

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Figure 2. IR absorption of the OH-groups in alkali silicate glasses. Difference spectra between samples with different water contents (numbers on curves = mole-% R_2O.
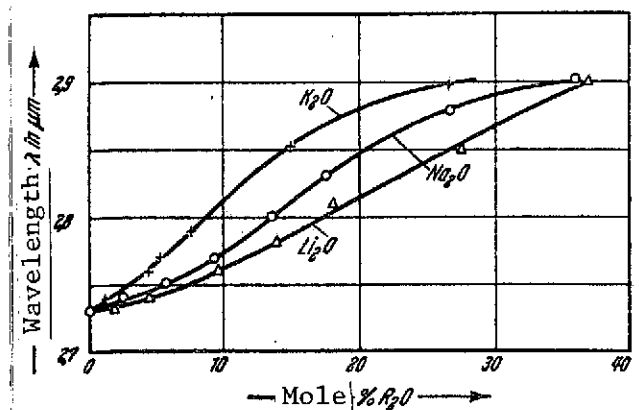
a) Li_2O, b) Na_2O, c) K_2O.

Figure 3. Position of the first OH-band in the IR spectrum of alkali silicate glasses.
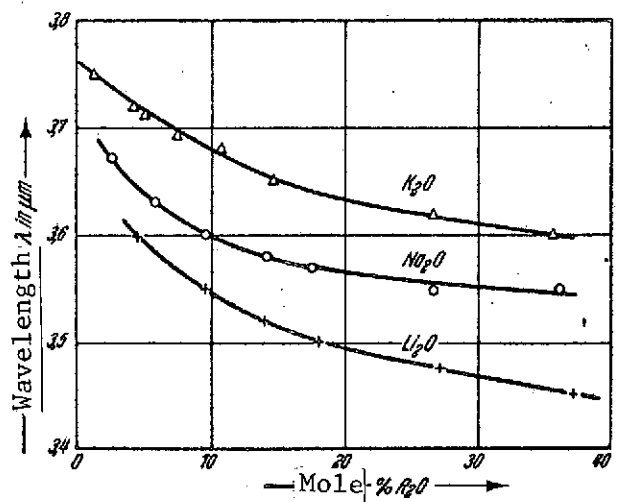
Figure 4. Position of the second OH-band in the IR spectrum of alkali silicate glasses.

The second OH-band at 3.6 µm can therefore be ascribed to the bonding types B,C,D, which differ only slightly in terms of energy, but differ considerably from type A. The small differences in the hydrogen bonding energies of the types B,C,D, as well as the manifold influence of the —OH...O-bridges by the irregular surrounding are the cause for the large width of the 2nd band.

The position of this band depends on the polarized state of the partner-oxygen of the H-bridge. If there is only one R+ cation in the immediate vicinity of this oxygen, then this one is least polarized and,therefore,the H-bridge bond the strongest, from which a longer wavelength of the OH-oscillation results. The more R+ ions enter into the neighborhood with increasing alkali content of the melt and the higher the field strength of R+ is, the stronger is the polarization of the partner-oxygen. The H-bridge,therefore,becomes weaker and the OH-band is shifted to shorter waves (Figure 4). In this way, it can be understood that the first OH-band is shifted to longer wavelengths with increasing alkali content, the second band, on the contrary, to smaller wavelengths.

The bonding type E schematically shows the very strong hydrogen bond discussed by Scholze [5] with which an isolated /145 $[SiO_4]$- tetrahedron is bound to the residual network. The corresponding OH-stretching frequency band appears always at 4.25 µm independent of the composition of the glass.

3.4. Ratio of the proportions of the OH-groups in the different bond-states

It could be shown in Section 3.1. that the attack of more alkali oxide on the SiO_2- network predominantly occurs at sites where the oxygens in Si—O—Si bonds are activated by neighboring alkali separation sites. This leads necessarily to a local accu-

mulation of alkali ions, i.e., to alkali "swarm" formation, which was first pointed out by Dietzel [20] and which was later proven by Oberlies [21] by the electromicroscopical detection of the phase separation in the micro-range. In the meantime, Vogel and collaborators [22] could also electromicroscopically detect this phase separation in glass which is free of the Tyndall-effect, besides others in the system Li_2O-SiO_2. In these glasses, therefore, alkali rich and SiO_2-rich domains exist beside each other.

It can now be expected that the attack of the water vapor according to reaction-Equation (9), in which a Si—O—Si-bridge is cleaved, will occur with higher probability in the SiO_2-domain, because in this case, mainly bridge-oxygens are present, whereas the availability of singly bound oxygens and exchangeable alkali ions is smaller. Accordingly, in this domain the bonding type A is favored, which is expressed in the first OH-band at 2.8 μm.

The attack according to reaction Equation (10) will predominantly occur in the alkali "swarm" domains, where the concentration of singly bound oxygens is high. Accordingly, the alkali availability for ion exchange R+ ↔ H+ is here the greatest and the number of the Si—O—Si-bridges is the smallest. In these domains, the bonding types B,C,D and E, which lead to the second and third OH-band at 3.6 and 4.25 μm, are predominantly present because of the large number of singly bound oxygens.

The intensity ratios of the OH-bands 1 and 2 + 3, as well as the ratio of the proportions of the OH-groups in the different types of bonds, can therefore yield information whether reaction (9) or (10) is favored during the attack of water vapor on the melt. The proportions of the dissolved "total water" in different bonding states are demonstrated in Figure 5, as they can be deducted from the IR spectra using the extinction coefficients calculated by Scholze [5] and in reference [9].
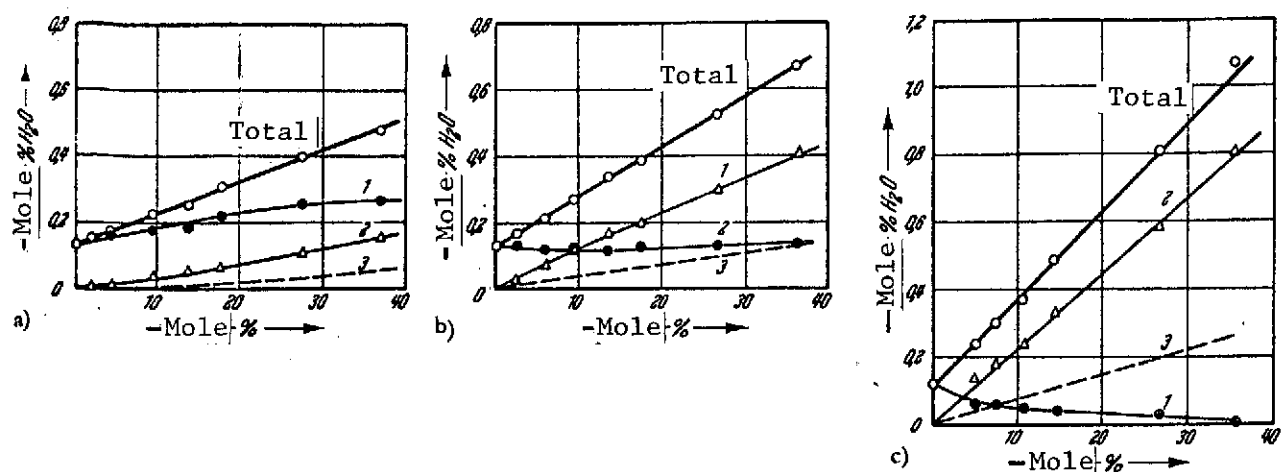
Figure 5. Distribution of the water dissolved in alkali silicate melts at pH_2O to different positions. Position 1: Free OH-groups, Groups 2 and 3: OH-group with H-bridge bonds.
a) Li_2O, b) Na_2O, c) K_2O.

3.5. Conclusions regarding the structure of alkali silicate melts

The relations presented in Figure 5 show clearly how the distribution of the alkali ions in the network of the glass is mirrored by the distribution of the OH-groups in different bond-states and in the spectrum resulting therefrom. The field strength or, from the standpoint of the electronic theory, the donor property of the alkali ions (see Section 3.1.) is decisive for this distribution and hence for the structure of the alkali silicate melts and glasses.

In the system Li_2O-SiO_2, the OH-proportions in positions 1, as well as in 2-3, increase with increasing Li_2O-content and, thereby, indicate that SiO_2-rich and alkali-rich domains exist beside each other. However, the separation-site oxygens in the alkali "swarm" domains are so extensively polarized by the relative strong Li+ cations that, besides the ion exchange Li+ ↔ H+

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[Equation (10)], the separation of Si—O—Si-bridges also occurs during the reaction of the glass with water vapor [Equation (9)]. The course of the curves in Figure 6 allows the observation that the ion exchange mechanism is only favored at a higher availability of Li+.

In the system Na_2O-SiO_2, the increase of the H_2O- solubility with the alkali content is almost exclusively due to the increased insertion of OH-groups according to reaction Equation (10), as demonstrated by the course of the curves in Figure 6. The almost Na_2O content independent proportion of the OH-groups in position 1 which do not have any singly bound oxygen in their surrounding and therefore must be present in a domain similar to silica glass, supports unequivocally a "swarm" structure of these glasses.

In the system K_2O-SiO_2, the number of OH-groups in positions 2 and 3 increases strongly with increasing alkali content whereas the number of OH-groups in position 1 decreases rapidly even at low K_2O contents. This shows that "swarm" formation is present only at low K_2O-contents whereas the K+ ions become more and more equally distributed when the K_2O-proportion increases. The donor effect of a potassium ion at a separation-site is hence so pronounced that not only the bridge oxygens at the other vertices of the same tetrahedron increase their formal charge δ, but also /146 other oxygens of the adjoining neighborhood become more reactive to a cation attack. Thereby the SiO_2-rich domains become smaller with addition of more K_2O and finally disappear with higher K_2O contents.

These conclusions are supported by the calculations of Urnes [23] who concluded on the basis of cryoscopic and X-ray crystallographic data that in alkali melts which are more acidic than the metasilicate, an equal distribution exists only in the systems Cs_2O-SiO_2 and Rb_2O-SiO_2. In the system K_2O-SiO_2, slight deviations

can already be detected which become much stronger in the systems Na_2O-SiO_2 and Li_2O-SiO_2 where they unequivocally indicate an alkali enrichment in "swarm" domains. A small deviating tendency in the system Na_2O-SiO_2 which becomes even more clear in the system Li_2O-SiO_2 was previously inferred by Dietzel [20], from the weak sigmoid shape of the melting curves of these systems.
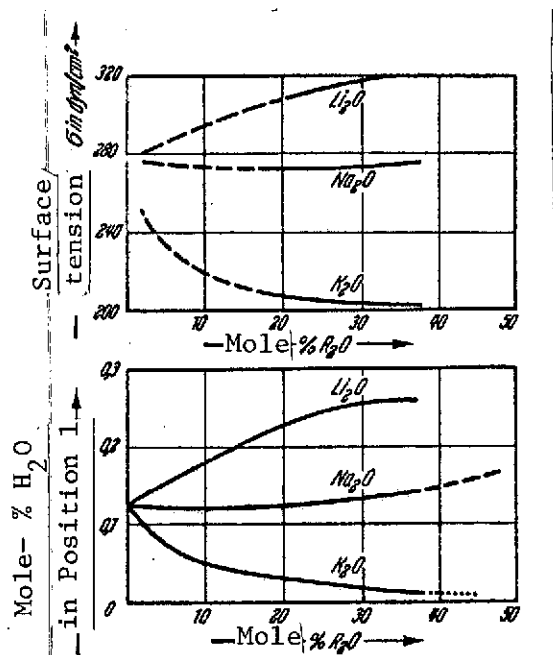
Figure 6. Surface tension of binary alkali silicate melts at 1300° C according to Shartsis and Spinner [24] and amount of water dissolved in position 1.

In this connection, it is interesting that the change of the surface tension, with the alkali content in the three alkali silicate systems, shows a distinct parallel to the water content in position 1, that is, to the proportion of the OH-groups inserted in SiO_2-rich domains, as shown in Figure 6. It therefore can be assumed that the surface tension of these melts is strongly influenced by the polarized state of the oxygens in the marginal zones of these domains resembling silicic acid.

3.6. Distribution of the alkali ions

The intensity ratios of the 2nd and 3rd OH-band at 3.6 and 4.25 µm, yield more detailed information about the different occupation states of the single $[SiO_4]$ tetrahedrons by alkali ions and the alkali distribution in the "swarm" domains, and their fine structure. Scholze [5] could calculate from a large number of results of measurements that in all silicate glasses,
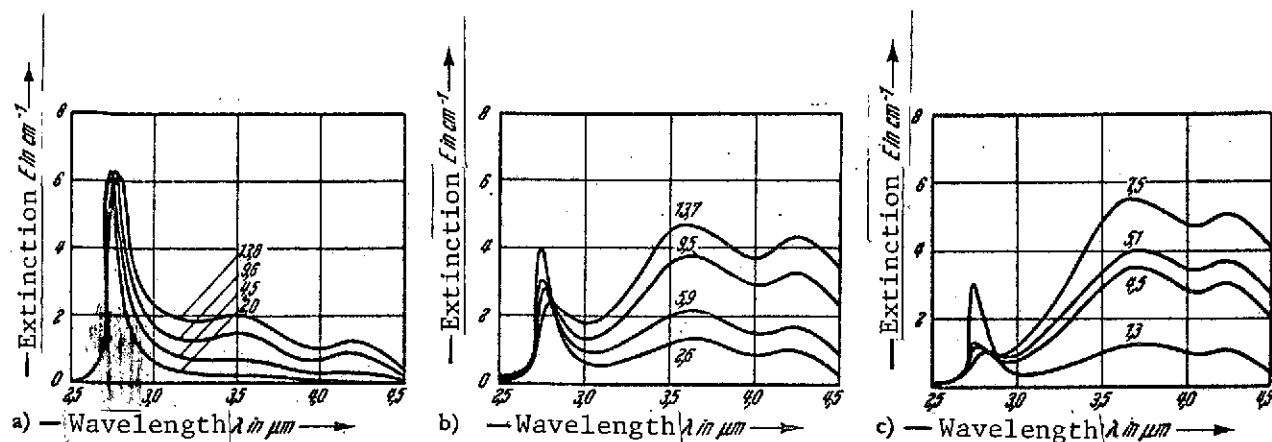
Figure 7. Infrared absorption of Oh-groups in alkali silicate glasses with low R_2O contents. Difference spectra between samples with different water contents. (Numbers on curves = Mole-% R_2O.

a) Li₂O, b) Na₂O, c) K₂O.

the ratio of the OH-concentrations, as indicated by the OH-bands 2 and 3, amounts on the average to 3:1, independent of the glass composition. This result is confirmed by our own measurements insofar as they showed that in the IR spectra of all tested binary and ternary silicate glasses the ratio of the intensities of the bands 2 and 3 is almost the same, independent of the kind and the concentration of the alkali, and alkaline earth ions and also independent of the total concentration of the Oh-groups of the glass. If one takes into account that — as schematically shown on Page 12, band 2 is caused by OH-groups with hydrogen bonds to $[SiO_4]$ tetrahedrons which are singly, doubly and triply occupied by alkali ions (bond-types B, C, D) and that band 3 is caused by H-bridges to fourfold filled tetrahedrons (bond type E), one easily arrives at the conclusion that an equilibrium exists in alkali silicate melts in which $[SiO_4]$-tetrahedrons (filled with one, two, three and four alkali ions corresponding to types B, C, D and E on Page 10, occur with about equal probability, because then the experimentally found 3:1 ratio of the OH-concentrations in positions 2 and 3 is fulfilled.

The question arises in which domain of the mixture this equilibrium exists. Figure 7 shows that the 2nd and 3rd OH-band also occur in the IR spectra of glasses with very low alkali contents. The appearance of the third band indicates that, in these glasses, isolated $[SiO_4]$-tetrahedrons do exist which are filled with four alkali ions (type E). Moreover, the constant ratio of the intensities of bands 2 and 3, which also here is independent from the alkali content, shows that $[SiO_4]$- tetrahedrons which are filled with one, two, three and four /147 alkali ions (types B, C, D, E) are not formed at high alkali contents only, but already at the beginning of the addition of alkali oxide to a SiO_2-melt, with about the same probability.

This picture of the structure also yields an explanation for the fact that the average Na-Na distance (independent from the alkali concentration) is about 2 Å, as Mueller-Warmuth and collaborators [25] calculated from measurements of the nuclear magnetic resonance. Mueller-Warmuth state the opinion that one hereby deals with the distance of a Na pair at a separation-site, that is, with Na+ ions which are situated on different (neighboring) $[SiO_4]$- tetrahedrons:

$$\begin{array}{ccc} | & Na^+ & | \\ -Si-O^- & O^--Si- \\ | & Na^+ & | \end{array}$$
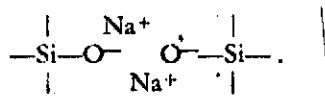
However, he further has to assume that the two separation-site oxygens and the corresponding Na+ ions cannot migrate far apart. However, the dramatic decrease of the viscosity of a SiO_2- melt by small alkali additions (which Dietzel [20] has already pointed out) indicates that an increased mobility and an easier flow of structural units is effected by the alkali separation-sites. During this flow process, not only the singly bound oxygens at a separation-site migrate apart, but simultaneously, also the two accompanying Na+ ions. On the other hand, the average distance of Na+ ions, which are present at the same
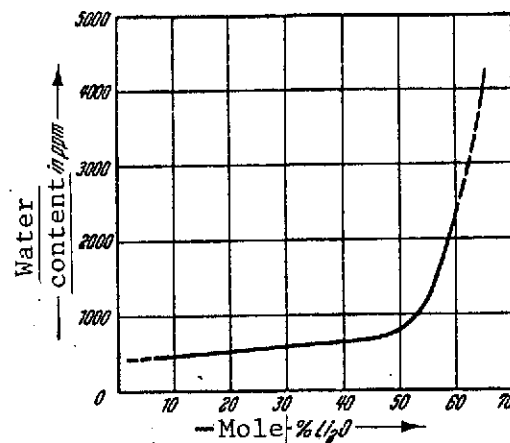
18

Figure 8. Solubility of water in Li_2O-SiO_2-melts at pH_2O = 146 mm Hg (according to Uys and King [13]).
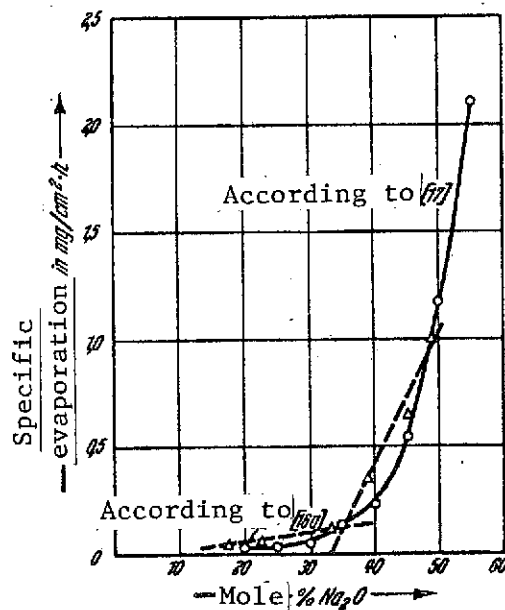
Figure 9. Evaporation of sodium silicate glasses in dependence of the Na_2O-content at 1300° C.

tetrahedron according to the above structural scheme and, therefore, in the same flow unit, will not change during the flow process.

At very high alkali contents, one has to take into account that free alkali oxide, which is not bound in the structure, also does exist in melts. In a completely homogeneous alkali distribution, these free R^+ and O^{2-} ions should only exist above the orthosilicatic composition, but do exist in "swarm" domains already at lower alkali contents if local enrichments are present. The free R^+ and O^{2-} ions can then react with water vapor according to

$$2\,R^+ + O^{2-} + H_2O \rightarrow 2\,(R^+OH^-)$$

(11)
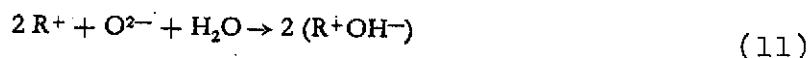
This reaction should be recognizable by a strong enhancement of the water vapor solubility, whereby it may be supposed that a new band appears also in the IR spectrum which is caused by the OH^- stretching frequency of the alkali hydroxide.

Our own experimental data do not yield information on this point because they are only good for alkali contents up to about 40 mole % R_2O. Uys and King [13], on the other hand, investigated the solubility in the system SiO_2 up to the orthosilicatic composition; their results are shown in Figure 8. Up to about 45 mole % Li_2O the solubility increases almost linearly, also quantitatively in very good agreement with out own measurements (9), and then increases steeper and steeper. An almost identical course is also exhibited by the evaporation of alkali oxide from alkali silicate melts, as the results of Turner and Preston [16] and the newer data of Dietzel and Merker [17] show in Figure 9. This is plausible since the free alkali oxide can evaporate much easier than the one which is bound in the structure.

From these experimental data, one has to conclude that the structural equilibrium exists between the different alkali filling steps of a $[SiO_4]-$ tetrahedron up to a content of about 40 mole% of alkali oxide, whereas at higher contents, especially in the alkali "swarm" domains, also free R+ and O^{2-} ions in the ratio R_2O do appear.

4.   SUMMARY

Regularities for the reaction of alkali oxide and water vapor with a silicatic melt follow from electron theory. In the reaction with one molecule of R_2O, a Si—O—Si-bridge is cleaved, i.e., a separation-site is created. The alkali atom at the separation-site acts as electron donor for the silicium atom. This entails that the bridge oxygen in the neighboring Si—O—Si-bond enhances its negative formal charge δ-, and thereby promotes a further alkali attack. This leads necessarily to an accumulation of alkali ions at the same tetrahedron and in the further course (of the reaction), to the formation of alkali "swarm" domains in   /148 a SiO_2-rich surrounding.

In the reaction of water vapor with silica glass, the cleavage of a Si—O—Si-bridge is initiated by a proton attack against the bridge-oxygen. Besides this, an ion exchange H+ ↔ Na+ occurs in alkali containing melts.

The equilibrium between these two reactions is determined by the polarized state of the bridge and separation-site oxygens. For the bond-state of the OH-groups inserted into the structure, five basic types result theoretically which are shown schematically on Page 9.

Bond-type A causes an OH-band at 2.8 μm in the IR spectrum, the types B,C,D cause an OH-band at 3.6 μm and type E a band at 4.25 μm. The bond-state of the OH-groups is, therefore, a sensitive

indicator for the structure of the near surrounding. From position and intensity ratios of the three OH-bands, as a function of the kind and concentration of alkali, the following conclusions can be drawn:

a) in lithium and sodium silicate glasses, alkali-rich and SiO_2-rich domains exist beside each other ("swarm" formation), whereas in potassium silicate glasses an approximation to a uniform distribution occurs with increasing K_2O-content.

b) a local decrease in reactive alkali oxide opposes an accumulation of alkali ions at a $[SiO_4]$-tetrahedron so that an equilibrium is established in which all four filling states of the tetrahedron with alkali ions, corresponding to the types B,C,D,E on Page 9 , possess about equal probability. This equilibrium exists already at very low alkali contents and is preserved up to about 40 mole % of R_2O, whereas at higher contents free R+ and O^{2-} ions appear in the ratio R_2O. The existence of these free, not structure bound R+ and O^{2-} ions is the cause for the strong increase of water vapor solubility and for the alkali evaporation at alkali contents of more than 40 mole % R_2O.

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